Removal Of Chromium (III) Ions from Simulated Wastewater Using Activated Carbon Derived from Periwinkle Shell

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Abstract- Agricultural wastes have shown potential for use as cheap and effective adsorbents for wastewater treatment. This study investigated the removal of Cr3+ ions from simulated wastewater using activated carbon derived from Periwinkle shell. The prepared adsorbent was characterized by analyzing some of its physicochemical properties, FTIR spectra and SEM micrographs. Batch adsorption experiments were conducted using initial metal ion concentration, adsorbent dosage and contact time as the process variables. Two common adsorption isotherms and two kinetic models were fitted to the adsorption data. The topography of the adsorbent's surface, available functional groups and its properties, indicate that the adsorbent is suitable for metal ion uptake from solution. The three process variables had positive effects on the percentage removal of Cr3+ ions. The adsorption process followed homogeneous monolayer coverage of the metal ions on the surface of the adsorbent, while chemisorption controlled the kinetics of the process. A mathematical model was derived and validated for the process. The maximum percentage metal ion removal was found to be 98.9 % at optimum values of 60 minutes, 93 mg/l of initial metal ion concentration and 6 g of adsorbent dosage. Periwinkle shell activated carbon is a cheap and effective adsorbent for the treatment of wastewater contaminated with Cr3+ ions.

Indexed Terms- Adsorption, Periwinkle shell, Chromium (III) ions, Characterization, Wastewater, Modeling

I. INTRODUCTION

The rapid development of industries involved in operations such as metal plating, mining, fertilizer production, tanneries, battery production, paper manufacture, pesticides production, etc. ([1], [2], [3]), has led to increasing discharge of heavy metal-laden wastewaters, directly or indirectly into the environment, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in industrial wastewaters include Zinc, Copper, Nickel, Mercury, Cadmium, Lead and Chromium [4].

Due to the non-biodegradable nature of these metal ions, they undergo transformations which can have health, environmental and economic impacts. To reduce the negative impacts of these contaminated wastewaters on the environment and health of humans and living organisms, treatment methods are required to remove these heavy metal ions before discharge into the environment. Some of the treatment technologies employed for the removal of heavy metals from wastewaters, include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electro dialysis and adsorption [5]. Some of these methods have inherent limitations such as high cost, generation of large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. Adsorption is relatively emerging as the potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent, is reversible and the adsorbent can usually be regenerated ([6]; [2];[5];[3]).

The high surface area, good porosity and the chemical nature of the surfaces of activated carbons [7], makes them suitable materials for the removal of heavy metals from industrial wastewaters. The use of low cost adsorbents derived from agricultural wastes, for the removal of heavy metal ions from industrial wastewaters is receiving attention from researchers.

The present study investigates the potential of using activated carbon derived from periwinkle shell, for the removal of Cr3+ ions from wastewater.

II. RESEARCH METHODOLOGY

Adsorbent preparation and characterization
The periwinkle shell samples used were washed and oven dried at 105ºC for 2 hours. The bone-dried samples were pyrolyzed at 700˚C for 1½ hours in the absence of air. The charred material was then activated using the method described in [8]. The activated carbon is shown in Figure 1. To characterize the adsorbent, selected physicochemical properties were determined [9]. The Fourier transform infrared (FTIR) spectrum and the Scanning electron micrograph of the adsorbent were also determined before and after adsorption.

Figure1. Produced Periwinkle shell activated carbon

Adsorbate preparation
The simulated wastewater was prepared by dissolving 1.417g of analytical grade Chromium (III) Sulphate in 1000 ml of deionized water. Different initial concentrations of Chromium (III) ion solutions were then prepared by appropriate dilution of the stock solution.

Adsorption experiments
The adsorption experiments were carried-out using the method described in [10]. Batch experiments were performed using contact time, adsorbent dosage and initial Chromium (III) ion concentration as the process parameters, whose effects on the percentage removal of the Cr^{3+} ions from solution were studied. In studying the effect of contact time, the adsorbent dosage and the initial metal ion concentration were kept constant at 6g and 70 mg/l respectively, while the

contact time was varied from 15 to 90 minutes. For the effect of adsorbent dosage, the contact time and the initial metal ion concentration were maintained at 60 minutes and 70 mg/l respectively, while the adsorbent dosage was varied from 2 to 10 g. The effect of the initial metal ion concentration on percentage metal ion removal was also investigated by keeping the contact time and adsorbent dosage constant at 60 minutes and 6g respectively, while the initial metal ion concentration was varied from 50 to 90 mg/l.

For isotherm studies, batch experiments were conducted by using 6 g of adsorbent dosage at different initial concentrations ranging from 50 to 90 mg/l in increments of 10 mg/l for 20 minutes with agitation rate of 150 rpm. While for the kinetic study, the adsorption experiments were carried-out by keeping initial metal ion concentration at 50 mg/l and adsorbent dosage at 6 g, while varying contact time in increments of 15 minutes ranging from 15 to 90 minutes. The concentration of the Chromium ions in the filtrate after each adsorption experiment was measured using the Atomic Adsorption Spectrophotometer (AAS).

The percentage of metal ion removed was determined from Equation 1, while the adsorption capacity of the adsorbent was calculated from Equation 2.

$$\%R = \left[\frac{c_0 - c_t}{c_0}\right] \times 100 \qquad \text{Equation 1}$$

$$q_e = \left[\frac{c_0 - c_e}{W}\right]V \qquad \text{Equation 2}$$

Where: C_o = Initial concentration of Cr^{3+} ions present in waste water before adsorption.
C_t = Final concentration of Cr^{3+} ions present after adsorption at time t.
C_e = Concentration of Cr^{3+} ions in the filtrate when equilibrium was attained.

V = Volume of stock solution (mL).
W = Mass (g) of adsorbent used.

Adsorption isotherms
The data from the adsorption process was fitted into the Langmuir and the Freundlich isotherm models. The Langmuir adsorption isotherm is based on a

homogeneous surface with identical active sites and restricted to a monolayer. It provides information on the metal ion uptake capabilities and the equilibrium adsorption behaviour. The Freundlich isotherm on the other hand, is an empirical expression based on multilayer adsorption on a heterogeneous surface of the adsorbent [11]. The Linear forms of the models were used in the study. The Langmuir model used is given in Equation 3, while the Freundlich model is presented in Equation 4.

$$\frac{C_e}{q_e} = \frac{1}{Q_{Ob}} + \frac{C_e}{Q_O} \qquad \text{Equation 3}$$

$$log q_e = log K_f + \frac{1}{n} log C_e \qquad \text{Equation 4}$$

The constants Q_o, b, K_f and n were evaluated from the slopes and the intercepts of the respective plots.

Adsorption kinetics

The pseudo first order and pseudo second order kinetic models were tested to evaluate the mechanism of the adsorption process. The linear form of the pseudo first order kinetic model used is given in Equation 5, while that of the pseudo second order model is presented in Equation 6.

$$log(q_e - q_t) = log q_e - \frac{K_1}{2.303} t \quad \text{Equation 5}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \text{Equation 6}$$

The values of the model parameters, q_e, q_t, k_1 and K_2 were also obtained from the slopes and intercepts of the respective plots [12];[13])

III. RESULTS AND DISCUSSIONS

Characterization and structural analysis of the produced adsorbent

The values of the analyzed physiochemical properties of the adsorbent are summarized below in Table 1. The adsorbent was slightly neutral with negligible moisture content, a high pore volume and a large surface area. All of these suggest an adsorbent with a high rate of adsorption and high adsorption capacity.

Table1. Characterization of periwinkle shell activated carbon

Physiochemical properties	Result
PH	7.02
Bulk Density (g/cm^3)	0.999
Temperature (ºC)	26
Moisture content (%)	0.012
Surface Area (m²/g)	618
Pore Volume\Porosity(cm³/g)	1.01

Fourier transform infrared spectra analysis

The Fourier transform infrared (FTIR) spectra, helps to identify the types of functional groups present in the adsorbent. The FTIR spectra of the adsorbent, before and after adsorption are shown in Figures 2 $m^2 g^{-1}$ and 3. The spectra show that the periwinkle shell activated carbon, has phenol, amine, alkane, hydroxyl, carboxyl, alkene and carbonyl functional groups. The presence of the oxygen rich hydroxyl and carboxyl functional groups improves the adsorption capacity of the adsorbent ([3];[14]). This is also a good indication that the adsorbent is suitable for interaction with heavy metals such as the uptake of Cr^{3+} ions.

The FTIR spectra of the adsorbent before and after adsorption showed peaks in the range of 500 – 4000 cm^{-1} as shown in Figures 2 and 3. After adsorption of Cr^{3+} ions, the spectrum exhibited an alteration around 525.71cm^{-1}, which was probably due to steric effect resulting from the adsorption of metal ions. In addition, there were band shifts from
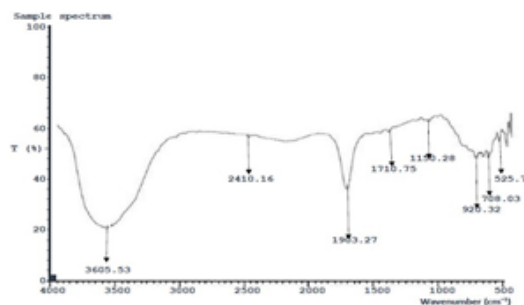

Figure 2: FTIR Spectrum of adsorbent before adsorption

3625.27 cm^{-1} to 3605.53 cm^{-1}, 2611.08 cm^{-1} to 2410.16 cm^{-1}, 1977.40 cm^{-1} to 1903.27 cm^{-1}, 1290.74 cm^{-1} to 1150.28 cm^{-1} and 941.60 cm^{-1} to 920.32 cm^{-1}. These shifts in frequency suggest that metal binding formations took place on the active sites of the adsorbent.
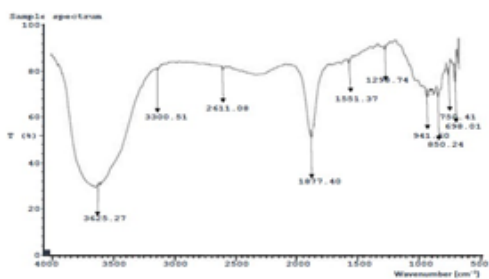
Figure 3: FTIR Spectrum of adsorbent after adsorption

Scanning electron microscopy (SEM) analysis
SEM analysis is useful in investigating the surface topography of the adsorbent. The morphology of the adsorbent before and after adsorption of Cr^{3+} ions can be evaluated from Figures 4 and 5. Figure 4, shows that before adsorption, the adsorbent possessed a smooth surface and uniform network structure with randomly distributed pores on the surface. These pores promoted the adsorption process and ensured high adsorption capacity of the adsorbent. After adsorption, the surface of the adsorbent shrunk, was rougher and showed fewer pore spaces (Figure 5), suggesting that the uptake of Cr^{3+} ions resulted in the observed changes in the surface of the adsorbent.
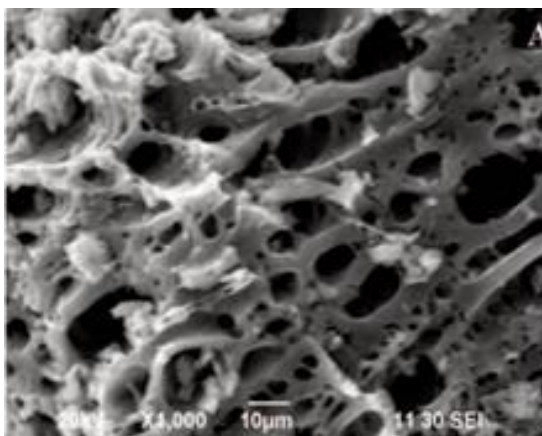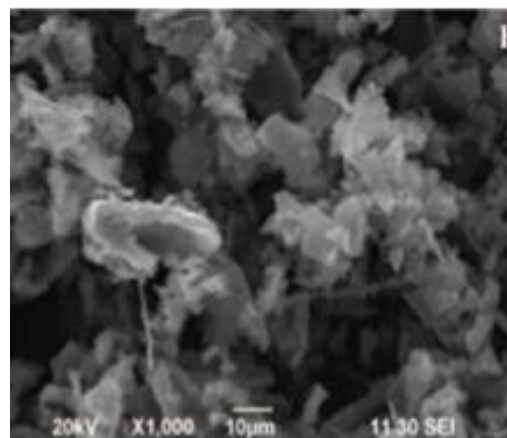

Figure 4: SEM before adsorption

Figure 5: SEM after adsorption

Effects of process variables
The percentage removal increased with increase in the initial metal ion concentration (Figure 6). This should be expected since increasing the initial metal ion concentration increases the driving force (concentration gradient) leading to increased metal ion adsorption. However, as the initial concentration of metal ions is increased further, the corresponding increase in percentage removal reduces. This is because the adsorption rate decreases as more of the active sites on the surface of the adsorbent are occupied by the metal ions. This explains the reduction in the slope of the plot of Figure 6, as initial metal ion concentration (Co) increases. This trend has been reported for related studies ([15];[16];[17]). The percentage removal also generally increased with increase in contact time (Figure 7) . Longer contact time allowed for more up-take of metal ions, but with time, the active sites on the surface of the adsorbent becomes saturated with the metal ions, thereby reducing the rate of further metal ion adsorption. Also, the electrostatic hindrance due to already adsorbed metal ions could contribute to the slower rate of adsorption observed as the contact time increases. Other workers reported similar observation ([16];[17]).
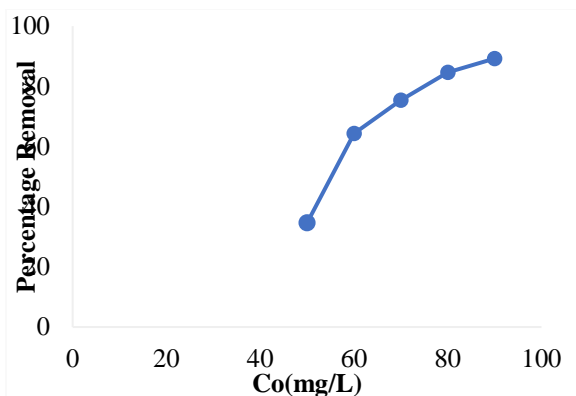
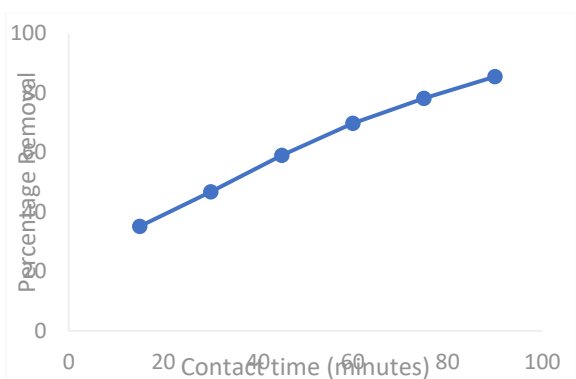Figure 6 ; Effect of initial metal ion concentration on percentage removal

Figure 7: Effect of contact time on percentage removal

The adsorbent dosage also positively affected the metal ions removal. The observed trend in Figure 8, can be attributed to the fact that that a greater quantity of adsorbent implies an increase in the number of active sites available for adsorption to occur and by extension, increased percentage removal. this is corroborated by the reports of [18] and [17].
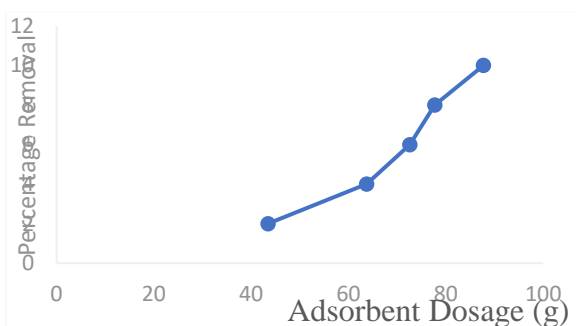

Figure 8: Effect of adsorbent dosage on percentage removal

Adsorption isotherms
Results of fitting the Langmuir and Freundlich models on the adsorption data is presented in Table 2. Both models appear to fit the data, but the Langmuir model which gave a higher R2 value (0.987) performed better than the Freundlich model in explaining the mechanism of the adsorption process. This implies that the adsorption process is restricted to a monolayer homogenous covering of the metal ions on the surface of the adsorbent. It further suggests that there is a homogenous distribution of active sites on the surface of the adsorbent having the same affinity for adsorption with no interaction between the adsorbed molecules [11]. This agrees with the findings of [18].

Table 2: Evaluated parameters and R^2 values for the Langmuir and Freundlich Isotherm models

Langmuir isotherm			Freundlich isotherm		
Qo mg/g	b l/mg	R^2	K_F (mg/g) $\cdot(L/mg)^{1/n}$	n mg/g	R^2
55.56	0.31	0.987	3.149	2.833	0.829

Adsorption kinetics
The R^2 values from the plots of the models, which is shown in Table 3, indicates that the pseudo second order kinetic model which gave a higher value (0.993),was better in describing the adsorption kinetics of the process. This suggests that the Cr^{3+} metal ions adsorption process was controlled by chemisorption, meaning that the Cr^{3+} ions were bound to active sites on the surface of the adsorbent via chemical bonds. Same was reported in [18] for the removal of Cr^{3+} ions using Sorghum bicolor as adsorbent, while [19], also indicated this trend for the sorption of some metal ions from aqueous solutions.

Table 3: Evaluated parameters and R2 values for the Pseudo first order and pseudo second order kinetic models.

Pseudo first order kinetic model			Pseudo second order kinetic model		
q_e mg/g	K_1 1/min	R^2	q_e mg/g	K_2 g/mg/min	R^2
10.23	0.0403	0.934	55.56	0.0008	0.993

Modeling and optimization
The model of the form in Equation 7 was proposed. The generalized reduced gradient tool in Excel Data Analysis Tool Pack was then used to determine the

parameters of the model. The developed model is given in Equation 8.

$$\%R = K\left(X_1^a \, X_2^b \, X_3^c\right)$$

Equation 7

$$Y = 0.02129\left(X_1^{0.40806} \times X_2^{1.23310} \times X_3^{0.51955}\right)$$

Equation 8

Where Y = percentage removal of metal ions
X_1 = Adsorbent dosage
X_2 = Initial metal ion concentration
X_3 = Contact time

The Solver Add-in on Excel was used to optimize Equation 8. The maximum percentage metal ion removal was found to be 98.9 % at optimum values of 60 minutes of contact time, 93 mg/l of initial metal ion concentration and 6 g of adsorbent dosage. The model was also experimentally validated by conducting additional experiments at various values of the process variables. The model validation plot of the experimental percentage removal against the model predicted percentage removal is given in Figure 9. An R^2 value of 0.9998 indicates the model is able to accurately predict the adsorption process
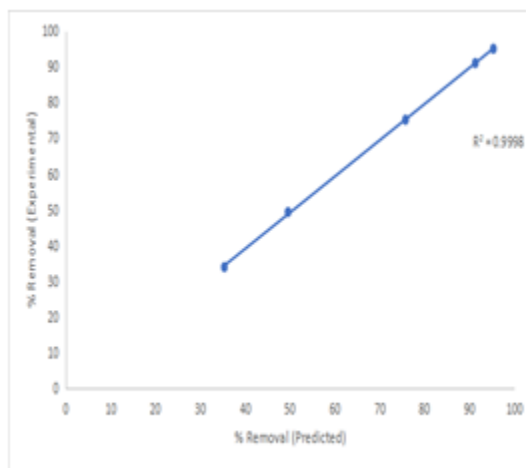

Figure 9: Experimental validation plot

CONCLUSION

Activated carbon derived from Periwinkle shell was used to remove Cr3+ ions from simulated wastewater. The physicochemical properties, the FTIR and SEM analyses of the adsorbent, suggest that the adsorbent is suitable for uptake of Cr3+ ions from wastewater. The study revealed that the adsorption process was influenced by the initial metal ion concentration, adsorbent dosage and contact time. These factors had positive effect on the percentage removal of metal ions. The mechanism of adsorption followed homogeneous monolayer coverage of the metal ions on the surface of the adsorbent, while the adsorption process was controlled by chemisorption. A mathematical model which could accurately predict the adsorption process has been derived and validated. The results obtained shows that activated carbon derived from Periwinkle shell, is an effective adsorbent for the removal of Cr3+ ions from wastewater.

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